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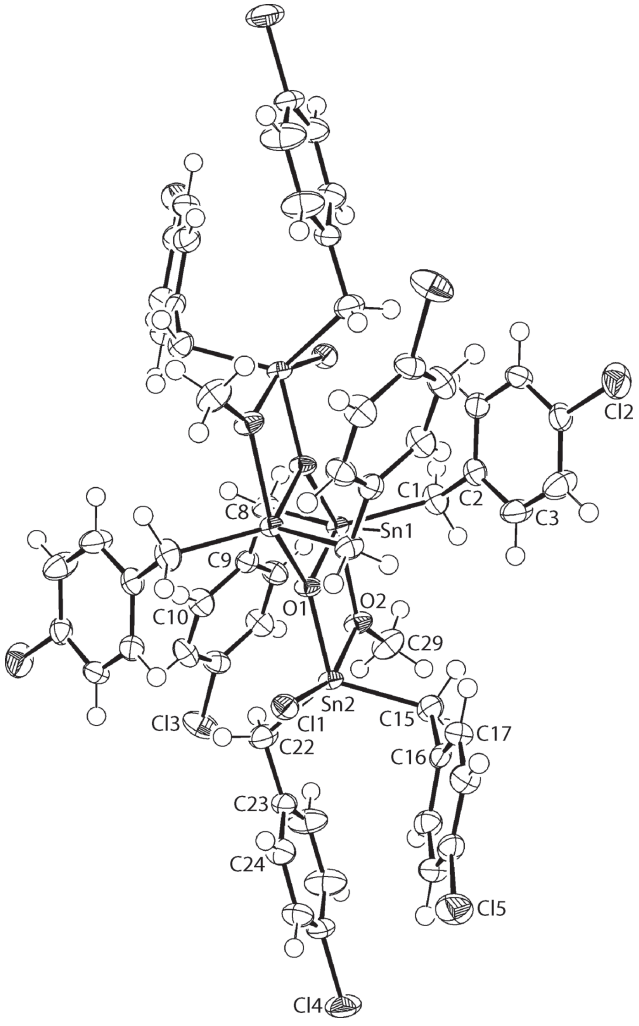
Crystal structure of octa(4-chlorobenzyl)-dichlorido-bis(μ_2-methanolato)-bis(μ_3-oxo)-tetratin(IV), $C_{58}H_{54}Cl_{10}O_4Sn_4$



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Abstract

$C_{58}H_{54}Cl_{10}O_4Sn_4$, monoclinic, $C2/c$ (no. 15), $a = 27.6269(8)$ Å, $b = 9.0623(2)$ Å, $c = 24.7099(7)$ Å, $\beta = 103.070(1)°$, $V = 6026.2(3)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0259$, $wR_{ref}(F^2) = 0.0671$, $T = 296(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.25 × 0.16 × 0.08 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	2.13 mm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX, ω
θ_{max}, completeness:	28.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	29767, 7513, 0.030
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 6540
$N(param)_{refined}$:	344
Programs:	Bruker [1], SHELX [2, 3], WinGX/ORTEP [4]

Source of material

All chemicals and solvents were used as purchased without purification. The melting point was determined on a Meltemp II digital melting point apparatus and was uncorrected. The IR spectrum was obtained on a Bruker Vertex 70v FTIR Spectrometer from 4000 to 400 cm^{-1}.

Di(4-chlorobenzyl)tin dichloride was synthesised by the direct reaction of 4-chlorobenzyl chloride (Aldrich) and metallic tin powder (Merck) in toluene according to a literature procedure [5]. The filtrate was evaporated slowly until a white precipitate was formed. The precipitate was recrystallised from a methanol/acetone mixture. The title compound was a side-product obtained from the slow evaporation of the solvent. Yield: 0.10 g (6%). **M.pt:** >553 K. **IR** (cm^{-1}) 1600 (m) ν(C—C), 1030 (m) ν(C—O), 481 (w) ν(Sn—O).

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
Sn1	0.28382(2)	0.09464(2)	0.51373(2)	0.01240(5)
Sn2	0.35949(2)	0.39261(2)	0.54324(2)	0.01416(5)
Cl1	0.32328(2)	0.64554(6)	0.52778(2)	0.01874(12)
Cl2	0.21795(3)	0.11632(8)	0.20353(3)	0.03083(15)
Cl3	0.44166(3)	0.05831(8)	0.78394(3)	0.03302(16)
Cl4	0.43851(3)	1.02366(7)	0.41920(3)	0.02916(15)
Cl5	0.59962(2)	0.65961(8)	0.68503(3)	0.03175(16)
O1	0.28876(6)	0.32071(18)	0.51904(6)	0.0151(3)
O2	0.36120(6)	0.15357(18)	0.54604(7)	0.0179(3)
C1	0.30167(10)	−0.0227(3)	0.44479(10)	0.0212(5)
H1A	0.3375	−0.0185	0.4497	0.025*
H1B	0.2932	−0.1254	0.4487	0.025*
C2	0.27957(9)	0.0201(3)	0.38591(10)	0.0171(5)
C3	0.30439(10)	0.1126(3)	0.35636(11)	0.0250(6)
H3	0.3341	0.1562	0.3746	0.030*
C4	0.28612(10)	0.1415(3)	0.30044(11)	0.0283(6)
H4	0.3035	0.2025	0.2813	0.034*
C5	0.24184(9)	0.0787(3)	0.27361(10)	0.0203(5)
C6	0.21583(9)	−0.0130(3)	0.30154(10)	0.0214(5)
H6	0.1859	−0.0552	0.2831	0.026*
C7	0.23493(9)	−0.0411(3)	0.35720(10)	0.0204(5)
H7	0.2174	−0.1027	0.3761	0.025*
C8	0.26934(9)	−0.0071(3)	0.58719(10)	0.0180(5)
H8A	0.2399	0.0378	0.5954	0.022*
H8B	0.2622	−0.1108	0.5796	0.022*
C9	0.31108(9)	0.0057(3)	0.63739(9)	0.0166(5)
C10	0.31552(10)	0.1290(3)	0.67192(10)	0.0214(5)
H10	0.2915	0.2026	0.6640	0.026*
C11	0.35463(10)	0.1448(3)	0.71744(10)	0.0229(5)
H11	0.3568	0.2274	0.7402	0.027*
C12	0.39037(9)	0.0363(3)	0.72869(10)	0.0201(5)
C13	0.38665(10)	−0.0894(3)	0.69660(11)	0.0228(5)
H13	0.4104	−0.1635	0.7053	0.027*
C14	0.34687(9)	−0.1040(3)	0.65100(11)	0.0199(5)
H14	0.3442	−0.1886	0.6293	0.024*
C15	0.40175(9)	0.3973(3)	0.48001(11)	0.0200(5)
H15A	0.4329	0.3457	0.4937	0.024*
H15B	0.3835	0.3441	0.4477	0.024*
C16	0.41286(9)	0.5497(3)	0.46241(10)	0.0167(5)
C17	0.38299(9)	0.6166(3)	0.41628(10)	0.0203(5)
H17	0.3569	0.5633	0.3946	0.024*
C18	0.39088(10)	0.7609(3)	0.40153(11)	0.0220(5)
H18	0.3708	0.8038	0.3702	0.026*
C19	0.42937(9)	0.8390(3)	0.43467(11)	0.0200(5)
C20	0.46052(9)	0.7758(3)	0.48062(11)	0.0216(5)
H20	0.4868	0.8292	0.5019	0.026*
C21	0.45181(9)	0.6317(3)	0.49424(11)	0.0207(5)
H21	0.4723	0.5886	0.5253	0.025*
C22	0.39069(9)	0.4209(3)	0.63046(11)	0.0227(5)
H22A	0.3698	0.4880	0.6456	0.027*
H22B	0.3905	0.3265	0.6489	0.027*
C23	0.44279(9)	0.4798(3)	0.64324(10)	0.0182(5)
C24	0.45245(9)	0.6287(3)	0.63588(11)	0.0224(5)
H24	0.4261	0.6917	0.6216	0.027*
C25	0.50026(9)	0.6849(3)	0.64925(11)	0.0230(5)
H25	0.5060	0.7849	0.6450	0.028*
C26	0.53920(9)	0.5898(3)	0.66893(11)	0.0216(5)
C27	0.53144(10)	0.4429(3)	0.67577(13)	0.0331(7)
H27	0.5582	0.3801	0.6889	0.040*
C28	0.48326(10)	0.3883(3)	0.66297(13)	0.0296(6)
H28	0.4780	0.2882	0.6677	0.035*
C29	0.40411(10)	0.0615(3)	0.55986(12)	0.0257(6)
H29A	0.4276	0.0910	0.5386	0.039*
H29B	0.3946	−0.0393	0.5516	0.039*
H29C	0.4190	0.0710	0.5987	0.039*

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.93–0.97 Å) and refined as riding with $U_{iso}(H) = 1.2$–$1.5U_{eq}(C)$. Owing to poor agreement, two reflections, i.e. (2 0 0) and (−2 0 2), were omitted from the final cycles of refinement. The maximum and minimum residual electron density peaks of 1.01 and 0.39 e Å^{-3}, respectively, were located 0.87 and 1.18 Å from the Sn1 and O1 atoms, respectively.

Comment

Hydrolysis products can be a regular synthetic outcome when performing reactions with diorganotin dichloride molecules in the presence of adventious moisture [6, 7]. In this context, the title organotin cluster [{[(4-ClPh)$_2$SnCl][(4-ClPh)$_2$Sn](OMe)}O]$_2$, (I), was isolated during a recrystallisation of (4-ClPh)$_2$SnCl$_2$. Herein, the crystal and molecular structures of (I) are described. We note that the structure of the unchlorinated benzyl analogue has also been reported in the literature [8].

The molecular structure of centrosymmetric (I) is shown in the figure (70% displacement ellipsoids; unlabelled atoms are related by the symmetry operation (i) $1/2-x$, $1/2-y$, $1-z$). The central Sn_2O_2 core is disposed about a centre of inversion and the endocyclic Sn1 atom forms similar Sn1—O1 [2.0555(16) Å] and Sn1—O1^i [2.1286(15) Å] bond lengths. The internal bond angles in the core, i.e. O1—Sn1—O1^i [73.04(7)°] and Sn1—O1—Sn1^i [106.96(7)°] indicate the shape of the core is that of a distorted rhombus. The oxo-O1 atom forms three Sn—O1 bonds, being also connected to the exocyclic Sn2 atom [Sn2—O1 = 2.0180(15) Å]. The methoxide anion bridges the Sn1 and Sn2 atoms, forming almost symmetric Sn—O2 bonds [Sn1—O2 = 2.1727(16) Å and Sn2—O2 = 2.1676(16) Å]. The penta-coordinate geometry for the Sn1 atom is completed by two methylene-C atoms of the benzyl substituents, and that for the Sn2 atom also by two methylene-C atoms as well as the chloride [Sn2—Cl1 = 2.4955(6) Å]. The C_3O_2 donor set about the Sn1 atom defines a highly distorted geometry. This is quantified by the value of $\tau = 0.33$ compared with 0.0 and 1.0 for ideal square-pyramidal and

trigonal-bipyramidal coordination geometries, respectively [9]. A distortion towards a trigonal-bipyramidal geometry is noted for the C_2ClO_2 donor set about the Sn2 atom for which $\tau = 0.56$. Overall, the sequence of three edge-shared Sn_2O_2 has the form of a shewed ladder.

No directional interactions occurring in the crystal of (I) are indicated in PLATON [10]. Reflecting the relatively large number of chloride atoms at the peripheral of the molecule there are many weak C—H···Cl interactions with the closest being a benzyl-phenyl-C—H···Cl(benzyl-phenyl) [C20—H20···Cl4^{ii}: H20···Cl4^{ii} = 2.83 Å, C20···Cl4^{ii} = 3.754(3) Å with angle at H20 = 171° for symmetry operation (ii) $1-x$, $2-y$, $1-z$] interaction. Also, there are weak Cl···Cl contacts [Cl3···Cl4^{iii} = 3.4441(10) Å for (iii) x, $1-y$, $1/2+z$]. Globally, the tetratin oxo clusters stack in columns along the *b*-axis and are connected into supramolecular layers in the *bc*-plane by Cl···Cl interactions. The aforementioned benzyl-phenyl-C—H···Cl(benzyl-phenyl) interactions connect the molecules along the *a*-axis direction.

The Hirshfeld surfaces and two-dimensional fingerprint (full and delineated) plots were also calculated in order to probe the molecular packing further. For this purpose, Crystal Explorer 17 [11] was employed using standard procedures [12]. This analysis points to the significance of Cl···H/H···Cl contacts which contribute 41.6% of all contacts to the Hirshfeld surface. The next greatest contribution comes from H···H [33.2%] contacts. Except for C···H/H···C contacts [14.9%], the remaining contacts contribute relatively small percentages, i.e. C···C [4.1%], Cl···C/C···Cl [3.2%] and Cl···Cl [3.1%].

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